The NIST "Real Fuels" Detailed Chemical Kinetic Combustion Model Database

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ABSTRACT

We report on the development status of the NIST "Real Fuels" Detailed Chemical Kinetic Combustion Model Database.[1] This unified Web site will provide the combustion community with a centralized source for detailed chemical kinetic models, along with supporting data and information. This site is currently in its developmental stage and NIST requests comments from the community to refine and improve its content, features, and capabilities. We see this site as one of a set of tools under development throughout the kinetics modeling community that are directed at next generation predictive reaction modeling capabilities. The intent for this site is to be complementary to other mechanism and modeling tools under development, to facilitate collaboration among the community with regard to process modeling, and to be integrated into developing infrastructure in the chemical sciences.

INTRODUCTION

The "Workshop on Combustion Simulation Databases for Real Transportation Fuels" identified a strong need for critically evaluated databases of thermochemical properties and elementary reaction rate coefficients to support detailed chemical kinetic models used in combustion simulations.[2] The lack of a centralized source for commonly employed, widely accepted datasets in the combustion community is somewhat in contrast to the atmospheric chemistry community where there are several centralized sources of regularly updated, critically evaluated datasets, including the IUPAC Subcommittee for Gas Kinetic Evaluation,[3] the JPL Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies,[4] and the Leeds Master Chemical Mechanism for degradation of tropospheric VOCs (volatile organic compounds).[5]

There are, of course, a number of general sources of thermochemical and chemical kinetic data (some evaluated, some simply compiled) that are regularly used in the development of detailed chemical models for combustion simulations, in addition to the numerous individual compilations and models by individual research groups in the field. Most of these are accessible on the internet. Commonly employed, general sources of this type of data include Burcat's Ideal Gas and Condensed Phase Thermochemical Database for Combustion,[6] Reaction Design's Chemkin Thermochemical Database,[7] and the GRI-Mech Combustion Model,[8] the NIST Chemistry Webbook,[9] and the NIST Chemical Kinetics Database.[10] Other sources of data provided by various individual research groups include the High Temperature Thermodynamics Database at Sandia National Laboratories,[11] the Combustion Chemical Kinetic Mechanisms at Lawrence Livermore National Laboratory,[12] and the Reaction Mechanism Library compilation at the California Institute of Technology.[13]

The existing evaluated databases most regularly employed in combustion modeling applications are not continually updated and, consequently, often are not current with regard to "best" values. One of the significant hindrances to rapid dissemination of such values is the vast amount of information now commonly employed in detailed chemical kinetic models for combustion – which regularly contain hundreds of species and thousands of reactions. The "database" aspect of the existing combustion model datasets – that is, managing the data – has not kept pace with the rapid advances in other aspects, such as the ability to predict thermochemical and chemical rate data with near "chemical accuracy" (4-8 kJ/mol) using quantum calculations, the ability to model realistic "reactor geometries" due the significant increase in desktop computational power, and the development of powerful tools for mechanism generation, analysis, and reduction. This is in addition to the relatively recent, significant increase in the detailed understanding of the many steps in hydrocarbon combustion processes on an elementary level. This has been brought about by improvements in both measurement science and computational methods.

A critically evaluated database for combustion would target important combustion species and reactions. For each species and reaction, such a database would provide recommendations based on the best individual or composite sets of data along with other relevant values available in the literature. This dataset would include recommendations from earlier reviews, data derived from experimental measurements, values predicted by quantum calculations, and estimated values. A commonly employed, centralized source for critically evaluated data for use in combustion applications would greatly reduce the extensive effort now required to trace and ascertain the quality and uncertainty of all of the thermochemical and chemical kinetic data commonly employed in combustion modeling.

In addition to a critically evaluated database for important combustion species and reactions, there is an urgent need for a compilation and centralized source of both comprehensive (or detailed) models as well as reduced chemical kinetic models that are used in combustion modeling applications. As indicated above, there are a number of individual sites where partial compilations of chemical kinetic models are available. However, there is no database devoted to chemical kinetic models that is readily available, nor is any organization known to be assembling such a database. In addition, some of the thermochemical and chemical kinetic data contained in these models is often not well documented or is contained in many different publications by different authors (that is, not explicitly included with the reaction set listing). Consequently, verifying the accuracy and relevance of the data is often difficult, as is updating all other values that may be dependent in some manner on new "best" values.

There are currently no widely employed standards for nomenclature, notation, and traceability for data contained in detailed chemical kinetic models. Such standards could greatly assist research in the area of developing and refining chemical kinetic models. The absence of such standards and the absence of a centralized repository for such data hinders facile comparison of models developed by different researchers. As a result, it is difficult to determine, for example, why two models may predict the same results for one set of conditions, but substantially different results for another set of conditions. The ability to easily make such comparisons is important for identifying important elementary reactions missing in a specific model and for identifying inaccurate rate coefficients. The establishment and maintenance of a detailed chemical kinetic model database will benefit the combustion modeling community and industry by facilitating improvement of existing models and their dissemination.

The purpose of the NIST "Real Fuels" Detailed Chemical Kinetic Combustion Model Database is to provide the combustion community with an online centralized source for detailed chemical kinetic models, along with supporting data and relevant information. This site is currently in its developmental stage and NIST requests comments from the community to refine and improve its content, features, and capabilities. We see this site as one of a set of tools under development throughout the kinetic modeling community that are directed at next generation predictive reaction modeling capabilities. The intent for this site is to complement other mechanism and modeling tools,[14,15] to facilitate collaboration among the community with regard to process modeling,[16] and to be integrated into developing infrastructure for chemical sciences.[17]

STATUS

The NIST "Real Fuels" Detailed Chemical Kinetic Combustion Model Database Web site[1] contains a number of different sections under development: Overview, Models, Reactions, Species, and Bibliography. As indicated above, this is a prototype and NIST seeks input and guidance from the combustion community with regard to its development.

The Overview section of the site provides general information about the site, about the organization of the data, and includes a description of the history and relevance of the site. This section also provides links to related sites at NIST and elsewhere. This includes sites providing thermochemical and chemical kinetic data, chemical kinetic models, and modeling-related codes and tools. The "Conventions Used" subsection provides a list of standard definitions, along with more detailed descriptions and examples, of chemical terminology relevant to this database. These definitions were adapted from a number of sources, including the IUPAC Compendium of Chemical Terminology (Gold Book).[18] In the field of chemical kinetics (and other fields), many "disagreements" often occur simply because one person is using a loose colloquial definition of a term, while another is using a more precise, standard definition. These standard definitions provide a basis for the reaction classification scheme employed in the Reactions section.

The Models section of the site provides (or will provide) the ability to obtain (or provide) descriptive information about specific chemical kinetic combustion models and to download (or upload) archival "flat file" listings of reaction sets. The goal is to have a number of well-documented annotated models with the ability to peruse for similar or related reactions, references, and other information. This section also includes a list of other models for many different systems that may be less well-documented (electronically), but are provided for archival purposes. The model systems are divided into general classes, (e.g., alkanes, aromatics, oxygenates, real fuels, etc.) and then further subdivided into individual systems (e.g., methane, butane, toluene, ethanol, dimethyl ether, JP-10, etc.). A model input form under development will guide entry of descriptive information about the model and the thermodynamic data and reaction set listings. This descriptive information includes bibliographic information (a literature reference) and conditions under which the model is relevant (e.g., temperature, pressure, equivalence ratio, reactor geometries, etc.). The descriptive information also includes the number of species and reactions in the model and "versioning" information such as whether the model is a new comprehensive mechanism, a refinement of a prior model, or a prior model with updated rate coefficients. The model form also provides links to "flat file" listings of the thermochemical data and reaction set, links to relevant documents (e.g., pdf files), and any links to authors' sites where more information may be obtained.

The Reactions section of the site will provide the capability to peruse well-documented annotated models, where reactions are classified by reaction type (e.g., C-H abstraction by OH). Links to species information, the NIST Chemical Kinetics Database, and bibliographic information are provided. A systematic reaction classification scheme is presented, along with a "simplified" notation for representing reaction types. This reaction classification scheme and notation build upon prior work by many others. The model reaction sets contained in this database can browsed or searched for related reactions, such as reactions involving the same species or similar species (e.g., n-alkanes, conjugated dienes, aromatics, etc.), or reactions with the same or similar reaction type (e.g., C-H abstractions by OH from a secondary carbon site). This is an important feature that facilitates comparison (and error checking) of rate expressions that are (or should be) similar. Descriptive information is also included such as identification of the datatype for the specific rate expression given (e.g., experimental, review, estimated by analogy, etc.) and links (where available) to more detailed information about the particular reaction. Eventually, the user will be able to search for all reactions in a particular detailed chemical kinetic model, compare forward and reverse rate expressions for specific reactions, compare rate expressions for reaction classes in a particular model and for specific reactions between different models, and compare rate expressions in a model with data contained in the NIST Chemical Kinetics Database.[10] Each reaction will include links to information about molecular properties, thermochemical, and other data for any species in a reaction. Some of this information will be contained directly in this database, and other information is provided simply through links to other databases at NIST (such as the NIST Chemistry Webbook[9] or the NIST Computational Chemistry Comparison and Benchmark Database[19]) or elsewhere. For each reaction a link is given to a citation in the bibliographic portion of the database.

The Species section of the site has capabilities such as the ability to browse/search species by species type (e.g., normal alcohols, sec-alkenyl radical, etc.). The concept of structure additivity relationships is integral to the development of detailed chemical kinetic models. There are few or no data for many important species and reactions. Consequently, group additivity methods for estimating properties of molecules, Evans-Polanyi type relationships for estimating rates of reactions, and other similar methodologies play important roles. In recognition of this, the proposed architecture of this database includes species (and reaction) classification schemes – somewhat in contrast to commonly employed datasets which index by non-chemical "attributes" such as CASNO's, chemical names, or molecular formula. All molecules in the database are (or will be) tagged with a classification scheme based on hierarchical chemical functionalities. For example, hydrocarbon-based systems are subdivided into acyclic aliphatics, aliphatics rings, and aromatics. These categories are then further subdivided into alkynes, alkenes, and alkanes, - then the degree of branching of the carbon backbone, and are subdivided with regard to valence (radicals, carbenes, etc.). Oxidized hydrocarbons are subdivided into carboxylic acids, aldehydes, alcohols, etc. and then further subdivided based on other functionalities in the molecules. Similar hierarchical classification (largely based on IUPAC rules) are employed for nitrogen-substituted and other compounds. A (semi) automated classification method based upon structural representations (such as MDL mol files) is one item to be developed.

In this section, a "species translator" is provided for the *ad hoc*, "pseudo-trivial," and often cryptical symbols commonly employed to represent molecules in detailed chemical models. The lack of a commonly employed nomenclature and notation makes comparisons between different models a difficult chore at best. A classification scheme and simplified notation for Polycyclic Aromatic Hydrocarbons (PAH's) is also presented enabling searching for PAH's by visually oriented structural patterns.

The Bibliography section of the site is to support data contained elsewhere in the database. It contains references pertaining to hydrocarbon combustion, relevant detailed chemical kinetic models, molecular and physical properties, thermochemical data, and chemical reaction rate data. The bibliographic database can also be searched by itself. A search returns a list of records, each displayed in a brief format. If desired, an individual record can be displayed in a full format. Each record has hyperlinks to other bibliographic records by the same author(s) or with the same keyword(s). There are also hyperlinks to species and reaction data abstracted from the original source.

SUMMARY

The goal of the NIST "Real Fuels" Detailed Chemical Kinetic Combustion Model Database is to provide the modeling community with a centralized source for detailed chemical kinetic models. In addition to the ability to simply download archival "flat file" listings of reaction sets (largely the current practice), the database will also provide more descriptive information about each model along with supporting data. An additional feature will be the ability to upload detailed models and supporting information, enabling efficient dissemination of improved models throughout the community. A particularly important emphasis of this database is the promotion of standards for nomenclature, notation, traceability, and communication in the modeling community. We hope that this database will assist research with regard to model optimization, enabling development of next-generation, validated models for use in combustion and other applications. The current site is a prototype and NIST seeks input and guidance from the combustion community with regard to its development.

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